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A METHOD FOR PRODUCING MIXED POLYMERS OF ETHYLENE

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A METHOD FOR PRODUCING MIXED POLYMERS OF ETHYLENE

[Verfahren zur Herstellung von Mischpolymerisaten des Äthylens]

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Claims /1*

1. A method for producing ternary mixed polymers of ethylene that contain more than 60 wt% ethylene, 1-20 wt% tert-butyl acrylate and/or tert-butyl methacrylate, and 1-10 wt% acrylic acid and/or methacrylic acid, incorporated by polymerization, by mixed polymerization of ethylene and tert-butyl acrylate and/or tert-butyl methacrylate in a reaction zone at temperature of -350°C and pressure over 800 atm, where the reaction mixture obtained at the end of the polymerization is sent to a cooling zone, in which a pressure under 500 atm and a temperature between 200 and 250°C are maintained, where the average residence time of the reaction mixture in the cooling zone and in the directly connected high-pressure product separation zone (A) is 2-10 min in accordance with Patent Application No. 25 24 274.4), which is characterized by the fact that the reaction mixture leaving the high pressure product separation zone (A) is sent through a low-pressure product zone (B) to a discharge extruder (C), where B and C are connected directly to each other without an isolating element and the fill height of the reaction mixture in B is adjusted through the discharge of C.

* [Numbers in the right margin indicate pagination of the foreign text.]

2. A method as in Claim 1, which is characterized by the fact that the temperature of the reaction mixture in the high pressure product separation zone (A) which is heated to 200-250°C, varies by a maximum ±2°C.

3. A method as in Claims 1 and 2, which is characterized by the fact that the fill height of the reaction mixture in B varies by a maximum of ±3%.

The primary patent ... (Patent Application No. P 25 24 274.4) concerns a method for producing ternary mixed polymers of ethylene that contain more than 60 wt% ethylene, 1-20 wt% tert-butyl acrylate and/or tert-butyl methacrylate and 1-10 wt% acrylic acid and/or methacrylic acid, incorporated by polymerization, by mixed polymerization of ethylene and tert-butyl acrylate and/or tert-butyl acrylate and/or tert-butyl methacrylate in a reaction zone at temperatures of 200-350°C and pressures above 800 atm, where the reaction mixture obtained at the end of the polymerization is sent to a cooling zone, in which a pressure under 500 atm and a temperature of 200 and 250°C are maintained, and where the average residence time of the reaction mixture in this cooling zone and in the immediately connected high pressure product separation zone (A) is 2-20 min. /2

In a preferred embodiment of the proposed method, the temperature of the reaction mixture in the high pressure product separation zone (A), which is between 200 and 250°C, varies by a maximum of ±2°C.

In a method as proposed in the parent application, one obtains homogeneous ethylene mixed polymers in which the copolymer content and the melt flow index are subject to only small variation. Very thin films that do not have any problematic irregularities such as specks and that are used as melt adhesive films can be produced from the homogeneous ethylene mixed polymers.

In spite of the improvements achieved in the parent application, it turns out that the formation of cross-linked inhomogeneous products in the equipment connected to the reactor cannot be excluded, especially with lengthy reactor run times. Thus, by the method of the parent application it is not possible to obtain material that is suitable for film production in an amount more than 50% of the output for reactor run times of more than 200 h. /3

This invention is based on the task of modifying the method in accordance with the patent application so that even after a lengthy run time predominantly products with [good] film properties, i.e., with good homogeneity, are obtained.

The task is solved in accordance with the invention by the fact that the reaction mixture leaving the high pressure product separation zone (A) is sent through a low pressure product separation zone (B) to a discharge extruder (C), where B and C are connected directly to each

other without isolating elements and the fill height of the reaction mixture in B is established through the discharge of C. Preferably the fill height varies by a maximum of ±3%.

Accordingly, the object of this invention is a method for producing ternary mixed polymers of ethylene that contain more than 60 wt% ethylene, 1-20 wt% tert-butyl acrylate and/or tert-butyl methacrylate and 1-10 wt% acrylic acid and/or methacrylic acid, incorporated by polymerization, by mixed polymerization of ethylene and tert-butyl acrylate and/or tert-butyl methacrylate in a reaction zone at temperatures 200-350°C and pressures above 800 atm, where the reaction mixture obtained at the end of polymerization is sent to a zone in which a pressure under 500 atm and a temperature between 200 and 250°C are maintained, where the average residence time of the reaction mixture in this zone and in the high pressure project separation zone immediately following it (A) is 2-10 min and where the reaction mixture leaving the high pressure product separation zone (A) is sent through a low pressure product separation zone (B) to a discharge extruder (C), where B and C are connected directly to each other without isolating elements and the fill height of the reaction mixture in B is established through the discharge of C.

According to an advantageous embodiment of the method, the temperature of the /4
reaction mixture in the high pressure product separation zone (A), which is heated to 200-250°C, varies by a maximum of ±2°C.

According to a preferred method, the fill height of the reaction mixture in B varies by a maximum of ±3%.

Homogeneous ternary mixed polymers that contain more than 60 wt% ethylene, 1-10 wt% acrylic acid and/or methacrylic acid and 1-20 wt% tert-butyl acrylate and/or tert-butyl methacrylate incorporated by polymerization are obtained. The ethylene mixed polymers produced by the method in accordance with the invention are used above all as hot melt glues, for example as thin films, for example for metals, ceramics, paper, textiles, plastics, wood, glass, etc. The melt flow index of the ethylene mixed polymers produced in accordance with the invention is 0.1-50, preferably 1-20 g/10 min (determined in accordance with STM-D-1238-65T at a temperature of 190°C and a ram weight of 2.16 kg).

A tubular reactor, which is easily used in continuous high pressure polymerization, serves as polymerization apparatus in accordance with the parent application. The ratio of the diameter to the length of the reaction tube is from 1 to 20,000 up to 20 to 20,000. The reaction tube is surrounded by a jacketing tube for a heat transfer agent. The reaction tube is divided into two independently heatable regions, of which the first region extends over two fifths of the length of the two and the second over the remaining three fifths of the length of the reaction tube. At the end of the reaction tube there is a valve, which serves to regulate the pressure in the polymerization space and also for discharge of the reaction material. At the end of this valve there is a jacketed tube in which the reaction mixture that has left the reaction tube is cooled to a

temperature between 200 and a maximum of 250°C, preferably 200-235°C. The pressure in this zone is less than 500 atm. The reaction mixture is then sent at this temperature to a high pressure product separation zone (A), also called a high pressure separator, in which nearly the same /5
pressure exists as in the jacketed tube in front of it. In this zone the polymer obtained in the reaction tube is separated from the unpolymerized monomers. The temperature of the reaction mixture in zone (A) which is 200-250°C, preferably 200-235°C, preferably varies by a maximum of ±2°C. The average residence time of the reaction mixture obtained at the end of the polymerization after being cooled to 200-250°C is 2-10 min. According to the method proposed in the main application P 25 24 274.4, the polymer, which still contains small amounts of monomer, is sent from the high pressure product separation zone (A) to a low pressure product separation zone (B), also called the low pressure separator, at pressures under 10 atm, and from it the polymer is sent to a discharge extruder (C).

According to the present invention the low pressure product separation zone (B) and the discharge extruder (C) are connected directly to each other without an isolating element and the fill height of the reaction mixture in B is established through the discharge of C. In a particular advantageous design of the process the fill height should vary by a maximum of ±3%.

The direct connection of B and C without an isolated element is understood to mean the coupling of B and C without interruption, so that no isolating device of any kind stops or inhibits the flow of the reaction mixture from B to C. Thus, no isolating device is used between B and C to control the status of the reaction product in B, but rather the fill height is exclusively controlled through the discharge rate of extruder C. The discharge rate of extruder C is determined by the rotary speed of the screw of extruder C. The status of the reaction mixture in B, the so-called fill height, can thus be controlled by the screw speed and kept constant to ±3%.

In contrast to the proposed method one obtains in accordance with the invention a considerably high fraction of product with good film quality, even with lengthy reactor run /6
times.

Example

The low pressure product separation zone of the polymerization apparatus described in the beginning is directly connected to the discharge extruder without an isolating element. The status in the separator is controlled with the rotary speed of the extruder and kept constant. The resulting polymers have very good homogeneity and good film properties. The quality of the polymers with increasing reactor run time is indicated in the following table:

(1) Laufzeit des Reaktors (Std.)	(2) Qualität des Polymerisats			
	(3) Homogenität	(4) Anzahl der Stippen		
		I (0,5-1 mm)	II (1-2 mm)	III (>2 mm)
100	(5) gleichmäßig	120	2	<0,5
200	(6) gut	125	4	<0,5
400		110	3	<0,5
600		120	3	<0,5
800		130	3	<0,5
1 000		115	2	<0,5
1 200		120	4	<0,5
1 600		125	2	<0,5
2 000		120	3	<0,5

Key:
1 Reactor run time (h)*
2 Quality of polymer
3 Homogeneity
4 Number of specks
5 Uniform
6 Good

Comparative example

The low pressure product separation zone of the polymerization apparatus described in the beginning is connected to the extruder via a 5-meter-long product line with an isolation device to control the status in the separation. The homogeneity of the polymers deteriorates with longer rector run time.

* [Editor's note: In the tables, commas in numbers represent decimal points.]

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(1) Laufzeit des Reaktors (Std.)	(2) Qualität des Polymerisats			
	(3) Homogenität	(4) Anzahl der Stippen		
		I (0,5-1 mm)	II (1-2 mm)	III (>2 mm)
100	(5) gut gleichmäßig	140	4	0,5
200	(6) mittel	180	10	2
400	(7) mittel-schlecht	350	40	10
600	(8) schlecht	800-1000	>100	20-40
>800	(8) schlecht	>1 000	>100	40-50

Key: 1 Reactor run time (h)
2 Quality of polymer
3 Homogeneity
4 Number of specks
5 Quite uniform
6 Average
7 Average-poor
8 Poor

The homogeneity of the ethylene mixed polymers given in the examples was measured on film 40 μm thick.

The films were made by extruding the ethylene mixed polymer obtained in the individual example at a temperature of 150°C. The takeup rate is 6.5 m/min, the neck length is 250 mm, and the expansion ratio is 1:2. The extruded film two passes through an optical device for continuous measurement of inhomogeneities in the film. 5 cm range is covered in the measurement of the doubled flat film, which has a width of 23 cm. Any homogeneity (specks or lumps in the film) generates an electrical pulse. The number of pulses, which corresponds to the number of specks, is summed over a measurement time of 400 sec for example (corresponding to a measured film area of 4.3 m^2). The inhomogeneities can be divided into 3 groups by establishing the sensitivity of the measurement differently, namely

I Speck size from 0.5-1 mm

II Speck size from 1-2 mm

III Speck size greater than 2 mm

The results are summarized in the table.

[Table not included in the original document.]